Solid State Sciences 24 (2013) 26–29

Contents lists available at SciVerse ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

Pseudobinary $Fe_4Ti_3S_8$ compound with a NiAs-type structure: Effect of Ti for Fe substitution

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ARTICLE INFO

Article history:
Received 9 April 2013
Received in revised form
10 June 2013
Accepted 4 July 2013
Available online 12 July 2013

Keywords:
$Fe_4Ti_3S_8$
NiAs-type structure
Preferential substitution
Magnetic ordering
Coercive field

ABSTRACT

The transition metal sulfide $Fe_4Ti_3S_8$ with 7:8 composition has been synthesized and studied by using X-ray diffraction, magnetization and electrical resistivity measurements. This compound exhibits a monoclinic crystal lattice (space group $I12/m1$). The substitution of Ti for Fe in Fe_7S_8 is found to result in a lowering of the Curie temperature ($T_C \approx 205$ K), in a larger value of the coercive field ($H_c \sim 9$ kOe at low temperatures) and in a substantial growth of the resultant magnetic moment per formula unit (μ_{FU}) in comparison with Fe_7S_8. An enhanced value of μ_{FU} is attributed to the preferential substitution of Ti in alternating cation layers. From the paramagnetic susceptibility measured within temperature interval (250–350) K, a reduced value of the effective moment per iron ($\mu_{Fe} \sim 2.4\mu_B$) was determined. The electrical resistivity of $Fe_4Ti_3S_8$ shows a non-metallic behavior and is affected by magnetic ordering.

1. Introduction

Binary transition metal chalcogenides of the general formula M_7X_8 (M = transition metal, X = chalcogen) have a layered NiAs-type superstructure with ordering of vacancies in some cation layers. For example, Fe_7S_8 (pyrrhotite) forms a hexagonal $2a_0 \times 2a_0 \times 3c_0$ superstructure (a_0 and c_0 are the lattice parameters of the NiAs unit cell) after rapid cooling from high temperatures, while slow cooling or low-temperature annealing leads to the formation of a monoclinic $(2\sqrt{3})a_0 \times 2a_0 \times 4c_0$ superstructure [1,2]. The structure of Fe_7X_8 consists of alternating layers of iron and chalcogen layers (sulfur or selenium). The vacancies are ordered in some iron layers, in a way that there is a layer of full Fe sites followed by a layer of Fe sites with vacancies. According to a neutron diffraction study [3], the magnetic moments of iron atoms in Fe_7X_8 are coupled ferromagnetically inside each iron layer, but coupled antiferromagnetically between adjacent layers. The presence of vacancies in some iron layers leads to incomplete cancellation of magnetic moments, resulting in the appearance of ferrimagnetism in Fe_7S_8 and Fe_7Se_8 systems below Curie temperatures of about 590 K [1,4] and 480 K [5], respectively. Unlike ferrimagnetically ordered Fe_7X_8, the Co chalcogenides Co_7S_8 and Co_7Se_8 having analogous crystal structures are reported to be Pauli paramagnets above 5 K [6]. It was pointed out that the absence of a magnetically ordered state in Co_7X_8 compounds may be associated with the delocalization of 3d-electrons because of the reduced interlayer distances, since the value of the c parameter in Co_7S_8 and Co_7Se_8 is about 10% less than that in Fe_7S_8 [7]. The substitution of Co for Fe in $(Fe_{1-x}Co_x)_7S_8$ and $(Fe_{1-x}Co_x)_7Se_8$ pseudobinary compounds leads to a lattice contraction along the c direction and to the disappearance of a magnetic coupling for $x = 0.6$ [8,9]. The magnetic properties of Fe_7X_8 were observed to be substantially affected even by low substitutions of Fe by other 3d metal atoms (up to 10 at.%) [10].

The aim of the present work is to study how the substitution of Ti for Fe in Fe_7S_8 will affect the crystal structure, physical properties and magnetic state. We have chosen the $Fe_4Ti_3S_8$ composition suggesting that the resultant crystal structure at this Ti amount will contain alternating layers with fully Fe sites and layers of Ti sites with vacancies. Alternating layers of titanium, sulfur and iron were observed in compounds Fe_xTiS_2 obtained by intercalation of iron atoms into TiS_2 matrix [11,12]. The parent TiS_2 compound has the CdI_2-type layered structure in which every other metallic layer in the c direction of the NiAs structure is missing. The intercalation of Fe atoms between S–Ti–S tri-layers in Fe_xTiSe_2 leads to the appearance of spin-glass or cluster-glass magnetic states at $x < 0.25$ and a long-range magnetic order at higher Fe concentrations [11]. In this work we describe the synthesis of the $Fe_4Ti_3S_8$ ternary (pseudobinary) compound and report the results of the crystal

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http://dx.doi.org/10.1016/j.solidstatesciences.2013.07.002

structure characterization, the measurements of magnetization and electrical resistivity.

2. Experimental

Polycrystalline $Fe_4Ti_3S_8$ was synthesized by solid-state reactions in an evacuated quartz tube. The starting materials were small pieces of 99.95% pure iodide titanium, sulfur (99.99%) and powder of carbonyl iron (99.98%). The tube with starting materials was gradually heated in a furnace from room temperature up to 950 °C (with one-day temperature steps at 200 °C, 400 °C and 600 °C), then the sample was kept for 2 weeks at temperature 950 °C followed by slow cooling to room temperature. The obtained sample was ground, compressed in tablets, sealed in a quartz tube under vacuum and then homogenized in a furnace for another week at 800 °C followed by slow cooling to room temperature. The obtained sample was studied by powder X-ray diffraction technique using a Bruker D8 ADVANCE equipped by a Goebel-mirror, selecting the Cu Kα radiation with a wavelength of λ Cu Kα = 1.5418 Å (weighted average of Cu $K_{\alpha 1}$ and Cu $K_{\alpha 2}$ radiation). The FULLPROF program (Le Bail fit) was used for analysis of the X-ray diffraction pattern.

The measurements of the magnetic susceptibility and magnetization were performed by means of a Quantum Design SQUID MPMS-XL-5 magnetometer and Quantum Design PPMS instrument equipped with the 90 kOe superconducting magnet in the temperature interval 2 K $\leq T \leq$ 350 K. The variation of the electrical resistivity with temperature was measured by the four probe method in the temperature range from 6 K up to 300 K.

3. Results and discussion

Fig. 1 displays the X-ray powder diffraction pattern obtained at room temperature for the $Fe_4Ti_3S_8$ compound. This pattern corresponds to the single-phase monoclinic structure described by space group $I12/m1$. The unit cell parameters of $Fe_4Ti_3S_8$ were determined as a = 5.9669(4) Å, b = 3.4396(3) Å, c = 11.5605(1) Å, β = 90.243(6)°, which corresponds to the $a_0\sqrt{3} \times a_0 \times 2c_0$ superstructure (where a_0 and c_0 refer to the primitive hexagonal unit cell of the NiAs structure). This structure differs from the 4C monoclinic structure of Fe_7S_8 probably owing to the presence of stacking faults caused by the substitution of Fe by Ti or by preferential substitution of Ti for Fe in alternating cation layers.

The variations of the magnetization with temperature measured on a $Fe_4Ti_3S_8$ polycrystalline sample at different magnetic fields and cooling/warming condition are shown in Fig. 2. The sharp change in the magnetization at the temperature $T_C \approx$ 205 K is indicative of the magnetic phase transition from a magnetically ordered state to the paramagnetic state with increasing temperature. This Curie temperature is substantially lower than that observed for Fe_7S_8 [3], which means that the substitution of Ti for Fe atoms reduces the exchange interactions.

Fig. 3 displays the temperature dependence of the inverse susceptibility, χ^{-1}, for $Fe_4Ti_3S_8$. In the temperature interval from 250 K up to 350 K the $\chi(T)$ dependence can be well represented by the expression: $\chi(T) = \chi_0 + C/(T - \theta_P)$. The value $\chi_0 = 4 \times 10^{-6}$ emu g^{-1} Oe^{-1} is a temperature independent term including the paramagnetic contribution of conduction electrons and the diamagnetic contribution from completely filled electron shells. The second term in the expression describes the Curie–Weiss contribution, where C is the Curie constant and θ_P is the paramagnetic Curie temperature. The shape of the χ^{-1} versus T dependence for our $Fe_4Ti_3S_8$ sample differs from the hyperbolic form observed for the ferrimagnetic compound Fe_7S_8 [13]. In contrast to Fe_7S_8, the θ_P value for $Fe_4Ti_3S_8$ is positive and equal to 220 K, which is slightly higher than the Curie temperature for this

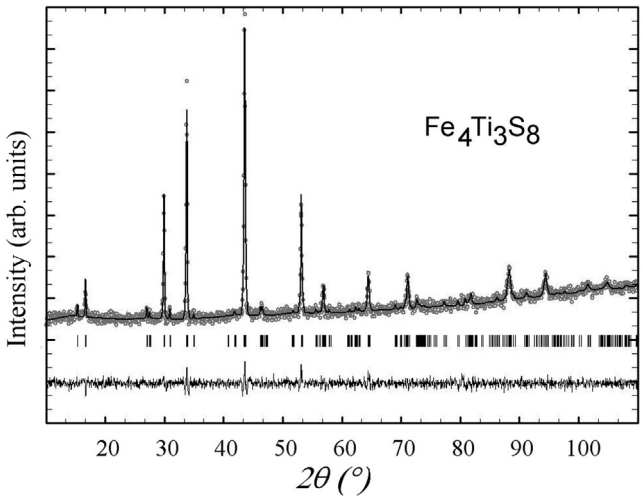

Fig. 1. Observed (symbols) and calculated (line) X-ray diffraction patterns for $Fe_4Ti_3S_8$ at room temperature. The difference between calculated and observed intensities is shown in the bottom of the figure. Vertical bars indicate the calculated Bragg peaks positions for a monoclinic structure described by the $I12/m1$ space group.

compound (T_C = 205 K). Such a value of θ_P implies the dominance of ferromagnetic exchange interactions in $Fe_4Ti_3S_8$. Assuming that Ti atoms have zero magnetic moment, the effective magnetic moment μ_{eff} per iron atom in our $Fe_4Ti_3S_8$ sample is estimated to be 2.4μ_B. This value of μ_{eff} is much smaller than the expected spin-only value for high-spin Fe ions (4.89μ_B for Fe^{+2} and 5.91μ_B for Fe^{+3}). The presence of Fe^{2+} and Fe^{3+} ions in Fe_7S_8 is still discussed. However, according to X-ray MCD [14,15] studies the Fe_7S_8 compound contains only Fe^{2+}, which implies that a simple ionic model is not applicable in this case. XMCD data [14,15] show that iron in Fe_7S_8 exhibits a large orbital contribution ($\sim$0.6μ_B) to the total magnetic moment. The 3d electrons of Fe ions in $Fe_4Ti_3S_8$ may be involved into bonds with sulfur atoms as in the non-substituted compound Fe_7S_8 in which a strong Fe–S hybridization has been revealed [14,15]. In $Fe_4Ti_3S_8$, the presence of the Ti–S and Fe–Ti hybridization effects can be suggested as well. The relatively high value of the temperature independent contribution χ_0 to the total magnetic susceptibility of $Fe_4Ti_3S_8$ may indicate the presence of a relatively high value of the density of electronic states at the Fermi level in this compound.

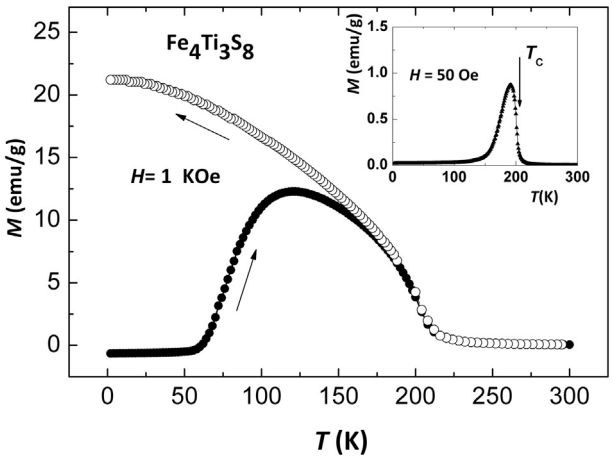

Fig. 2. The temperature dependences of the magnetization for $Fe_4Ti_3S_8$ measured in the field 1 kOe at ZFC and FC regimes. Inset shows the $M(T)$ dependence measured on the zero-field cooled sample at H = 50 Oe.

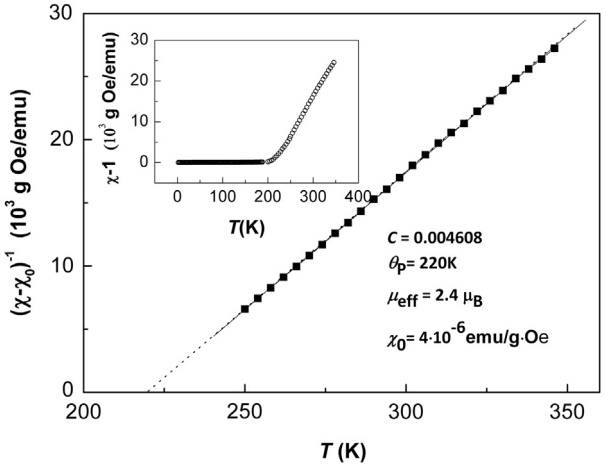

Fig. 3. Fitting the temperature dependence of the reciprocal susceptibility to Curie–Weiss law for $Fe_4Ti_3S_8$ in the temperature interval 250 K–350 K. Inset shows the χ^{-1} versus T dependence for whole temperature range from 2 K up to 350 K.

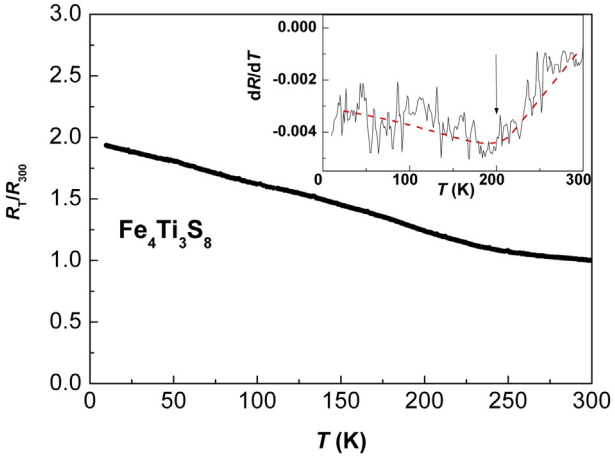

Fig. 5. Temperature variation of the relative electrical resistance of a $Fe_4Ti_3S_8$ polycrystalline sample. Inset shows the dR/dT versus T dependence. The dashed line is drawn by eye.

The field dependences of the magnetization measured at different temperatures on $Fe_4Ti_3S_8$ sample are presented in Fig. 4. As is seen, the magnetization curve measured at $T = 250$ K, i.e. above Curie temperature, exhibits a Brillouin-shape, while $M(H)$ dependences measured below $T_C = 205$ K show a ferromagnetic-like behavior, the presence of a spontaneous magnetization and hysteresis which increases with decreasing temperature. At $T = 2$ K, the coercive field H_c is determined to be about 9 kOe that seems to be rather high for the compounds in which the magnetism is determined by iron since the iron based materials usually demonstrate a soft magnetic behavior. From the data presented in Fig. 4, we estimated the saturation magnetization $M_S = 47$ emu g^{-1} at $T = 2$ K by using the law of approach to saturation [16]. This value corresponds to 5.25μ_B per formula unit (μ_{FU}) which is substantially higher than $\mu_{FU} = (2.03–2.53)\mu_B$ reported for Fe_7S_8 in the literature [3,17]. The enhanced value of the saturation magnetization in our $Fe_4Ti_3S_8$ compound in comparison with non-substituted Fe_7S_8 may be ascribed to the non-statistical distribution of substituents (Ti atoms) over the crystal lattice. As was mentioned above, the presence of the ferrimagnetic order in Fe_7S_8 is related to antiparallel alignment of the magnetic moments of iron atoms in successive

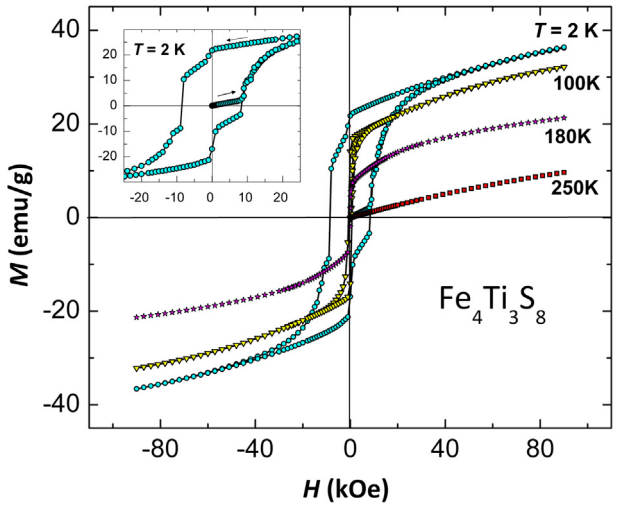

Fig. 4. Field dependences of the magnetization for $Fe_4Ti_3S_8$ measured at various temperatures. Inset shows $M(H)$ at 2 K in details.

layers, combined with the distribution of iron vacancies in every second layer, which results in the incomplete compensation of the moments. If the iron atoms in Fe_7S_8 are replaced by titanium equally in all metallic layers, the resultant magnetization of the $Fe_4Ti_3S_8$ compound should be lower than for Fe_7S_8. But if we assume that all the Ti atoms substitute Fe atoms in only one sublattice (or at least if the distribution of Ti in the two sublattices is substantially different), we will have a Fe-rich sublattice with high magnetization and the other Ti-rich sublattice with a small magnetization. Such a preferential substitution of Ti in alternating metal layers may cause the increase of the μ_{FU}. The question about the distribution of Ti and Fe atoms in $Fe_4Ti_3S_8$ is of considerable importance, but is a difficult matter to resolve it using the X-ray analysis because of closeness of the atomic numbers of Ti and Fe.

In order to characterize further the properties of $Fe_4Ti_3S_8$ we measured the temperature dependence of the electrical resistivity on a polycrystalline sample (shown in Fig. 5). As can be seen the electrical resistivity exhibits a non-metallic behavior in the temperature range below 300 K. The room-temperature resistivity, ρ_{300}, for $Fe_4Ti_3S_8$ is obtained to be 3.57×10^{-6} Ω m, i.e. of the same order of magnitude as observed for pyrrhotite [18]. As shown by Sakkopoulos [19], the iron sulfides FeS_x ($1 \le x \le 1.25$), in particular the pyrrhotite Fe_7S_8, exhibit a metal–semiconductor transition which is observed at the same temperature where the magnetic phase transition from the paramagnetic to the magnetically ordered state occurs. In order to check whether the magnetic ordering affects the behavior of the electrical resistivity in our compound we have plotted the derivative as a function of temperature (see inset in Fig. 5). As it turned out, the dR/dT versus T dependence exhibits a minimum at temperatures around the Curie temperature $T_C = 205$ K, which indicates that the appearance of a magnetic order below T_C influences the transport properties of this compound as well.

4. Conclusions

By using the method of solid-state reactions the pseudobinary compound $Fe_4Ti_3S_8$ with a layered NiAs-type structure has been synthesized. Unlike the non-substituted Fe_7S_8 compound having a 4C superstructure, the $Fe_4Ti_3S_8$ compound is observed to exhibit the 2C superstructure. Such a difference in crystal structures may be associated with the presence of stacking faults and preferential substitution of Ti for Fe in alternating metal layers. The lattice

parameter $a_0 = 3.439(6)$ Å for $Fe_4Ti_3S_8$ is found to be nearly the same as for Fe_7S_8 (3.439 Å) [4], while the parameter $c_0 = 5.780(2)$ Å for $Fe_4Ti_3S_8$ exceeds slightly the c_0 value for Fe_7S_8 (5.704 Å) [4].

The magnetization measurements performed for $Fe_4Ti_3S_8$ have shown that the magnetic properties of Fe_7S_8 are noticeably affected by the substitution of Ti for Fe. As it could be expected, $Fe_4Ti_3S_8$ exhibit a substantially reduced magnetic ordering temperature ($T_C \approx 205$ K) in comparison with Fe_7S_8 having a ferrimagnetic order below $T_C \sim 590$ K [1]. However, at low temperatures, the $Fe_4Ti_3S_8$ compound shows the hysteresis loop with a coercive field as large as 9 kOe and an increased value of the saturation magnetization per formula unit $\mu_{FU} = 5.25\mu_B$ which is nearly twice higher than the value for Fe_7S_8. The high coercivity of $Fe_4Ti_3S_8$ originates apparently in the increased orbital moment of Fe. The presence of the enhanced saturation magnetization in $Fe_4Ti_3S_8$ we consider as an indication of a non-random distribution of iron and titanium in cation layers. A non-random distribution of different 3d-metal atoms was revealed in some other pseudobinary transition metal sulfides with the NiAs-related structures (see Ref. [20], for instance). The neutron diffraction measurements are strongly desirable to confirm our suggestion about the preferential distribution of Fe and Ti in alternating cation layers in $Fe_4Ti_3S_8$.

A reduced value of the Fe effective magnetic moment ($\mu_{eff} \sim 2.4\mu_B$) obtained for $Fe_4Ti_3S_8$ from the susceptibility measurements in the paramagnetic region (up to $T = 350$ K) can not be described in a local-moment model. It is worth to mention that according to neutron diffraction measurements iron atoms in Fe_7S_8 have a lower value of the ordered magnetic moment (ca. 74%) than the expected spin-only moment [3]. A significant decrease in the ordered moments (to ~50%) from the spin-only value was also observed in the $Ni_xCr_{3-x}S_4$ system with the NiAs structure type [21]. A low value of μ_{eff} for Fe in $Fe_4Ti_3S_8$ may be associated with the Fe–Ti and Fe–S hybridization effects.

The room temperature electrical resistivity of $Fe_4Ti_3S_8$ is observed of the same order as of Fe_7S_8. For the Fe_7S_8 case, the growth of the resistivity with decreasing temperature below T_C was attributed to the appearance of energy gaps in electron spectrum owing to the antiferromagnetic ordering [19]. As to the ferromagnets with metallic-type conductivity, they usually demonstrate a decrease in the resistivity with lowering temperature below the Curie temperature. Therefore, a non-metallic behavior of the resistivity and the minimum observed in the (dR/dT) dependence near T_C for our sample indicate that, there is a similarity of magnetic orders in both $Fe_4Ti_3S_8$ and Fe_7S_8 compounds. Bearing in mind the results obtained for the non-substituted compound Fe_7S_8 which shows a metallic-type behavior of the resistivity at $T > 590$ K [19], i.e. above the magnetic ordering temperature, one can suggest that, positive temperature coefficient of the resistivity will be observed in our $Fe_4Ti_3S_8$ sample at higher temperatures (higher than the temperature limit in our measurements).

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (projects no 13-02-00364 and 13-02-96038) and by the government of Sverdlovsk region.

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